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A LOW GASSING IGNITER MIXTURE FOR VARIOUS PYROTECHNIC DELAY COMPOSITIONS

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

A LOW GASSING IGNITER MIXTURE FOR VARIOUS PYROTECHNIC DELAY COMPOSITIONS

Prepared by:

E. Eugene Kilmer

Approved by: Anson D. Solem
Chief, Explosion Dynamics Division

ABSTRACT: Mixes of zirconium and lead monoxide have been investigated for use as hot wire sensitive gasless igniter mixes for igniting gasless delay powders. A (50/50) zirconium/lead monoxide composition is sensitive to hot wire ignition; it reliably initiates molybdenum and manganese base delay mixtures; it acts essentially as a gasless delay igniter for such delay mixtures used in systems having delays up to several seconds in time. It does not act gasless when igniting long burning tungsten delay mixes. It will not satisfactorily ignite all delay compositions so that its selection for use must be based on knowledge of its specific behavior with the particular delay composition contemplated.

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This report presents information concerning the search for a "gasless" igniter to be used in electro-explosive devices. The work was carried out in the Explosion Dynamics Division of the Explosions Research Department, U. S. Naval Ordnance Laboratory, White Oak, Maryland, in connection with Wep Task RUME 3E000/212 1/F008 10 004, Problem 016, Applied Research for Underwater Detonators. The results of this investigation are intended for the information and use of the Naval Ordnance Laboratory and should be of interest to others working with electro-explosive devices.

W. D. COLEMAN
Captain, USN
Commander

C. J. Aronson

C. J. ARONSON
By direction

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A LOW GASSING IGNITER MIXTURE FOR VARIOUS PYROTECHNIC DELAY COMPOSITIONS

Introduction

1. The designs of electro-explosive devices (EEDs) containing "gasless" delays have almost exclusively used primary explosives heated by a bridgewire to effect initial reaction. Primary explosives, when they react, produce liberal quantities of gaseous combustion products. If these gases are allowed to materially increase the internal pressure of the EED, the burning rate of the gasless delay, which is pressure sensitive, is considerably increased over its rate at ambient pressure, and inefficient use of the delay (with respect to time/length) results. In addition, if the internal gas pressure is not controlled, time uniformity may not be obtained.

2. To overcome these difficulties practical designs have allowed for venting the primary explosive gases through vent holes to the exterior or have incorporated a fully contained internal vent chamber (1). The former expedient reduces the shelf life of the EED in moist environments and also prevents potting of the EED. The latter solution overcomes the moisture and potting difficulties but requires increased volume or length (for the vent chamber) and this space in a weapon system is often at a premium.

3. Another method of overcoming the problem would be to eliminate the primary explosive and substitute an igniter material sensitive to ignition by a hot wire and having combustion products which are essentially gasless. Such igniter materials have not been generally available. Two possibilities, however, exist:

Metal acetylides.

"Gasless" mixes similar to the gasless delays but with sufficient sensitivity to be initiated by hot wires.

The acetylides had been previously investigated (2) but abandoned because of their extreme static sensitivity and difficulty of preparation. Gasless igniter materials of sufficient sensitivity were unknown; however, some gasless igniter mixes, A-1A for example (3), were known to be marginally close to the sensitivity desired*

*A-1A could be initiated by a hot wire some of the time but not always. In some cases the wire could be burned out without initiating the A-1A.

4. The Universal Match Corporation in 1959 was assigned a problem under Contract NOrd 13466, Task 2, to develop hot wire sensitive gasless igniter mixes for use in non-vented delay systems. The results of their work are summarized in their final contract summary report (4). In brief, they found a number of mixes which could be ignited by hot wires. They centered their testing on the most promising; mixes of boron and lead dioxide and mixes of zirconium and lead dioxide. The boron mix was found to introduce appreciable non-uniform delays itself so zirconium/lead dioxide was the final igniter material selected. When it was used in non-vented delays appreciable reduction in time over the vented system resulted.

5. The work reported herein is a continuation of the work started at the Universal Match Corporation. It was hoped to obtain a sensitive gasless igniter capable of being incorporated into non-vented delays without appreciably decreasing the burning time below that of identical vented items. It has been found that a (50/50) zirconium/lead monoxide igniter mix acts as if it were gasless when igniting molybdenum and manganese base mixes in systems with delays up to several seconds. This mix, however, does not satisfactorily ignite all delay compositions and affects the burning times of long burning tungsten base delays in obturated systems.

Selection and Preparation of Mixes

6. After reviewing the work performed by the Universal Match Corporation and all other pertinent literature and information, it was decided that mixtures of zirconium and lead monoxide would be investigated. An approximate stoichiometric mixture of these ingredients, (17/83) Zr/PbO, as well as several oxygen deficient combinations were prepared. The zirconium powder conformed to specification JAN-Z-399A. The lead monoxide was reagent grade obtained from Merck and Co. It was finer than 325 mesh. For reasons of safety, mixing was performed with the ingredients wet. The wetting fluid was ethyl acetate. Quantities of 10 grams or less were wetted with the fluid and mixed in a Waring blender for twenty minutes. The mixtures were then filtered and dried in an oven.

Selection of Final Mix for Further Tests

7. The selection of the final mix for further testing was based on two criteria:

- The ignition sensitivity at a selected size hot wire.

The rapidity of the combustion sensed by a phototube detector.

Preliminary sensitivity tests were conducted by pressing the mixtures about a 0.0004-inch diameter Tophet-C wire, 0.050 inch long, and then determining, by a few exploratory tests, the potential needed on a 1-microfarad capacitor to cause samples to fire. The results of this testing are given in Table 1. From this table it can be seen that the (20/80), and (50/50) Zr/PbO mixes could be ignited without sufficient difference in sensitivity to choose between them. The (95/5) Zr/PbO mix could not be fired even at 6 microfarads and 250 volts, and was thus eliminated.

8. The (20/80), (40/60), and (50/50) Zr/PbO mixes were than subjected to hot wire ignition testing in which the light ouput was viewed as a function of time using a photoelectric detector tube and an oscilloscope. Typical traces for the three mixes are shown in Figure 1. The (20/80) Zr/PbO mix showed no output for the full sweep of the oscilloscope, which was 5 milliseconds in these tests, although the mix, of course, was ignited. The inherent delay was felt to be too long and the burning, which finally did occur, too erratic for further consideration of this mix as an igniter material. The (40/60) mixture and the (50/50) mixture ignited within the sweep time; however, the (40/60) mixture showed a rather slow build-up in intensity while the (50/50) mixture showed an even, rapid build-up to its final intensity. On the basis of these results it was decided to use only the (50/50) mixture for further testing.

Testing in Delay Devices

9. Tests in delay devices, both obturated and vented, were conducted with delay mixes of various burning rates. Comparisons were made between burning times in the vented and non-vented devices. Two types of test vehicles were chosen for these tests.

For the obturated condition the fast burning compositions (molybdenum and manganese based mixes (5), (6)) were tested in the unit shown in Figure 2, and the slow burning composition (tungsten based mix (5)) was tested in a larger body shown in Figure 3. The test devices were loaded such that there was no internal free volume for venting of gases during burning.

The vented devices were identical to the obturated ones shown in Figures 2 and 3 except that the charge holder was reduced in diameter and a vent hole 0.025 inch in diameter was drilled in the delay body slightly above the igniter level to allow gases to escape to the exterior.

10. On the basis of preliminary tests, the igniter mix was loaded at 10,000 psi. The initiator assembly contained 30 milligrams of (50/50) Zr/PbO igniter mix. The quantity of igniter used for the fast burning molybdenum and manganese base mixes was 100 milligrams while the slow burning tungsten base delay composition required 250 milligrams of the igniter mix. The delay compositions were loaded at 30,000 psi and the units tested over a temperature range of -65°F to + 160°F. The energy from a 1-microfarad capacitor charged to 60 volts was used to produce ignition and the ability of the mixture to ignite the delay compositions and the delay times were determined. Table 2 summarizes the results observed.

The manganese delay compositions were reliably initiated over the temperature range +160°F to -65°F in both the obturated and vented systems.

In the case of the molybdenum base delays, there was no significant difference in the observed delay times between the obturated and vented systems.

For the manganese delay compositions there was a small reduction of the burning time in the obturated system.

The slow burning tungsten base delay composition was ignited satisfactorily in the obturated system but in the vented system failures occurred at the igniter-delay mix interface. The failures were probably due in part to the loss of pressure caused by the venting. There was a considerable reduction in time in the obturated system as compared to the vented system. This can be seen from the tests conducted at 160°F where all items ignited properly. The table shows also that ignition reliability at the igniter-delay interface is a function of the operating temperature.

Sensitivity to Hot Wire Ignition

11. Two methods were used to determine the sensitivity of the (50/50) zirconium/lead monoxide mix to ignition by a hot wire.

The first was a capacitor discharge Bruceton type test (7) using a fixed 1-microfarad capacitor and a variable potential.

The second was a variable-amplitude, constant-current, run-down type test.

12. The data for the capacitor discharge test are shown in Table 3. The mean firing potential was determined to be 57.4 volts which corresponds to an energy of 16,500 ergs. If the assumed log normal distribution is correct, the 99.9% firing point is at 63.1 volts corresponding to an energy of 19,900 ergs.

13. The constant-current data were obtained on two groups of elements containing the igniter mix. The results are shown in graphical form in Figure 4. From this curve it can be seen that the current characteristics of the two groups were rather uniform, that virtually no primers fire below approximately 340 milliamperes, and that virtually all can be expected to fire above 420 milliamperes. The number at each point plotted on the curves indicates the number of igniters tested at this point.

Conclusions

14. From the experiments conducted it is concluded that the (50/50) zirconium/lead monoxide igniter mix acts as if it were "gasless" when igniting molybdenum and manganese base mixes having times up to several seconds. When igniting long burning tungsten base delays, there is an appreciable reduction of time in the obturated system over that of the vented system.

15. This igniter mix does not satisfactorily ignite all delay compositions; auxiliary igniters such as A-1A on top of the delay column may be necessary in some cases. The igniter mix may be satisfactorily ignited from hot wires. The energy required is somewhat more than that needed for sensitive primary explosives.

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Table 1

Preliminary Tests of Firing Voltages for Zr/PbO Compositions

Zr/PbO Weight Ratio	Loading Pressure (psi)	Capacitance (mfd)	Potential (volts)	Result*
95/5	10,000	6	250	Failure
50/50	10,000	1	48-50	Fire
50/50	20,000	1	53-54	Fire
40/60	10,000	1	48-50	Fire
40/60	20,000	1	53	Fire
20/80	10,000	1	50-65	Fire
20/80	20,000	1	60-65	Fire

* The lower voltage is the lowest value at which any sample was observed to fire. The upper voltage is the lowest value at which all samples tested fired.

Table 2

Observed Delay Times for Delay Compositions
Ignited from (50/50) Zirconium/Lead Monoxide·Igniter Mixture

Type of Delay Powder	Inverse Burning Rate (sec/in)	Delay Column Length (inches)	Calculated Delay Time (seconds)	Temp.	OBTURATED Sample Size	OBTURATED Mean Delay Time (seconds)	VENTED Sample Size	VENTED Mean Delay Time (seconds)
Molybdenum base	0.22	0.270	0.059	165°F	5	0.0654	5	0.0661
	0.22	0.270	0.059	Room	5	0.0716	5	0.0710
	0.22	0.270	0.059	-65°F	5	0.0825	5	0.0805
Manganese base	2.53	0.233	0.589	160°F	10	0.519	10	0.539
	8.02	0.243	1.949	160°F	10	1.50	10	1.84
	13.23	0.265	3.51	160°F	10	2.54	10	2.79
	2.53	0.233	0.589	Room	10	0.565	10	0.578
	8.02	0.243	1.949	Room	10	1.63	10	1.89
	13.23	0.265	3.51	Room	10	2.66	10	2.77
	2.53	0.233	0.589	-65°F	10	0.585	10	0.674
	8.02	0.243	1.949	-65°F	10	1.62	10	1.99
	13.23	0.265	3.510	-65°F	10	2.82	10	2.95
Tungsten base	39.4	0.822	32.39	160°F	10	15.41	10	31.55
	39.4	0.822	32.39	Room	10	17.25	10	*
	39.4	0.822	32.39	-65°F	10	19.34	10	**

* 7/10 failed at the igniter-delay interface.
**10/10 failed at the igniter-delay interface.

Table 3

Determination of the Firing Characteristics of Igniter Mix (50/50) Zr/PbO by the Bruceton Sensitivity Method

i	Volts h_i*	n_i Fire X's	n_i Failure O's	in_i	i^2	i^2n_i
6	61	1	0	0	36	0
5	60	3	1	5	25	25
4	59	4	3	12	16	48
3	58	7	4	12	9	36
2	57	5	7	14	4	28
1	56	5	5	5	1	5
0	55	0	5	5	0	0
$c = \log h_o = 1.74036$		Sum	Sum	Sum=A		Sum=B
$d = \Delta \log h = 0.007$		Nx = 25	No = 25	A = 53		
			$No^2 = 625$	$A^2 = 2809$		B = 142

$$m = c + d\left(\frac{A}{Nx} - \frac{1}{2}\right) \text{ or } = c + d\left(\frac{A}{No} + \frac{1}{2}\right)$$

$$m = 1.74036 + .007\left(\frac{53}{25} + \frac{1}{2}\right) = 1.75870$$

Antilog m = 57.4 Volts

Capacitance = 1 mfd.

$$M = \frac{NB - A^2}{N^2} \quad \text{Use Nx or No as above}$$

$$M = \frac{25(142) - 2809}{625} = 1.186$$

From Table or Graph p. 51-54 AMP Report No. 101.1R

$$\sigma = d\,(0.05 + 1.6M)$$
$$\sigma = .007(.05 + 1.6(1.186))$$
$$\sigma = 0.01363$$

Prob. Firing	K	Kσ	m+Kσ	E (% point) =5CV^2 *
.001	-3.090	-0.042117	1.71658	$5(1)(52.0)^2 = 13,520$
.500				$5(1)(57.4)^2 = 16,470$
.999	+3.090	+0.042117	1.80082	$5(1)(63.1)^2 = 19,910$

*C - microfarads
V - volts
E - ergs

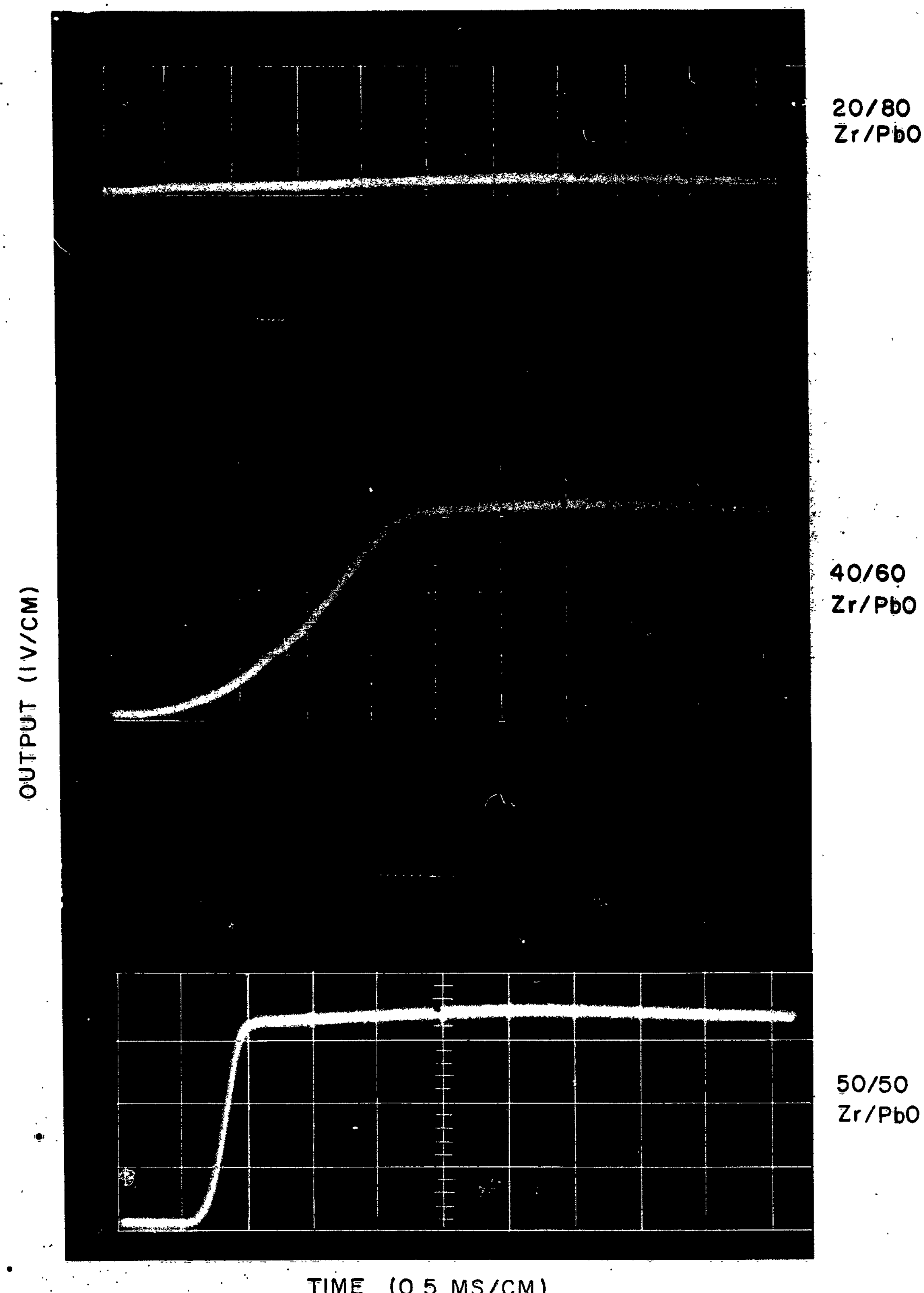

FIG. 1 LIGHT OUTPUT DURING BURNING OF SEVERAL ZIRCONIUM/LEAD MONOXIDE IGNITION MIXTURES

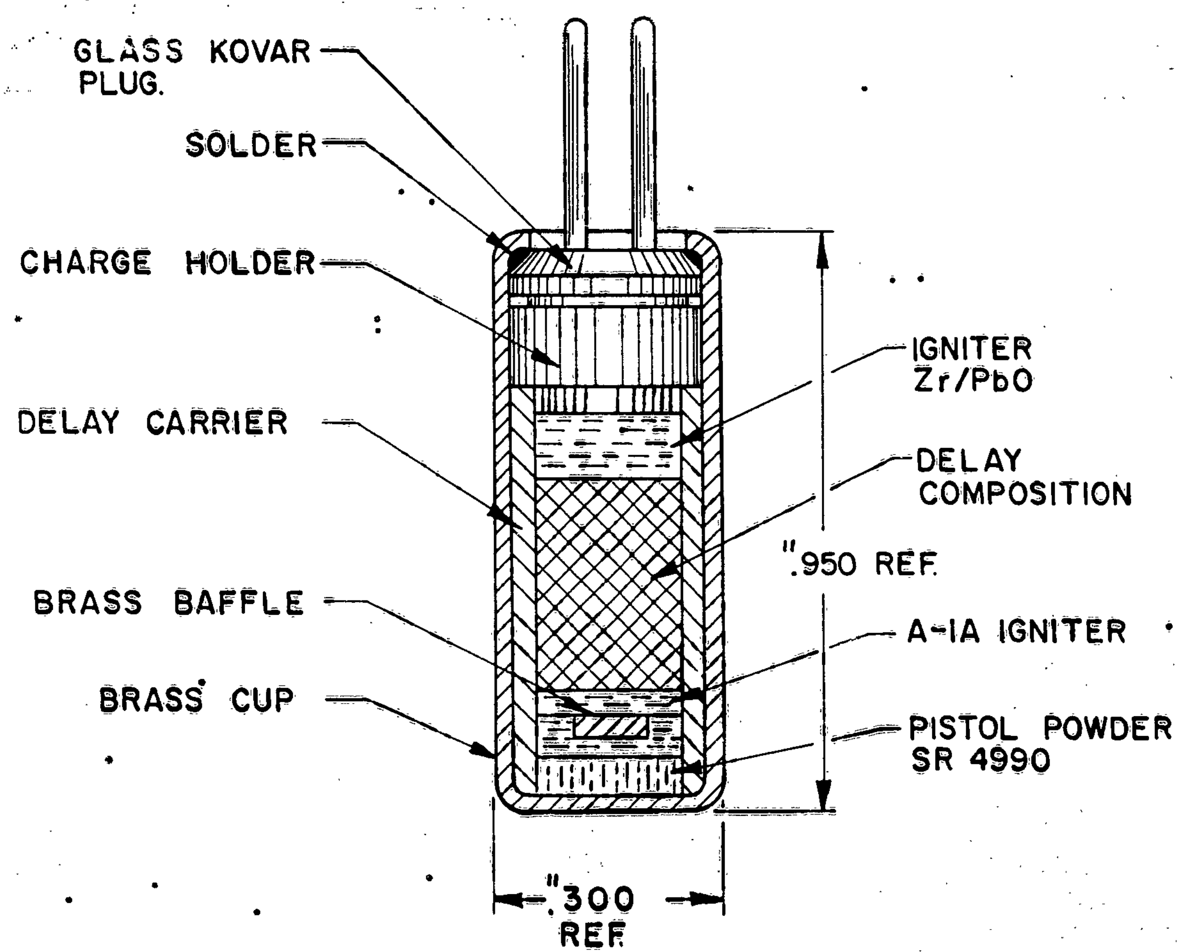

FIGURE 2. THE TEST VEHICLE USED FOR TESTING THE FAST BURNING DELAY COMPOSITIONS.

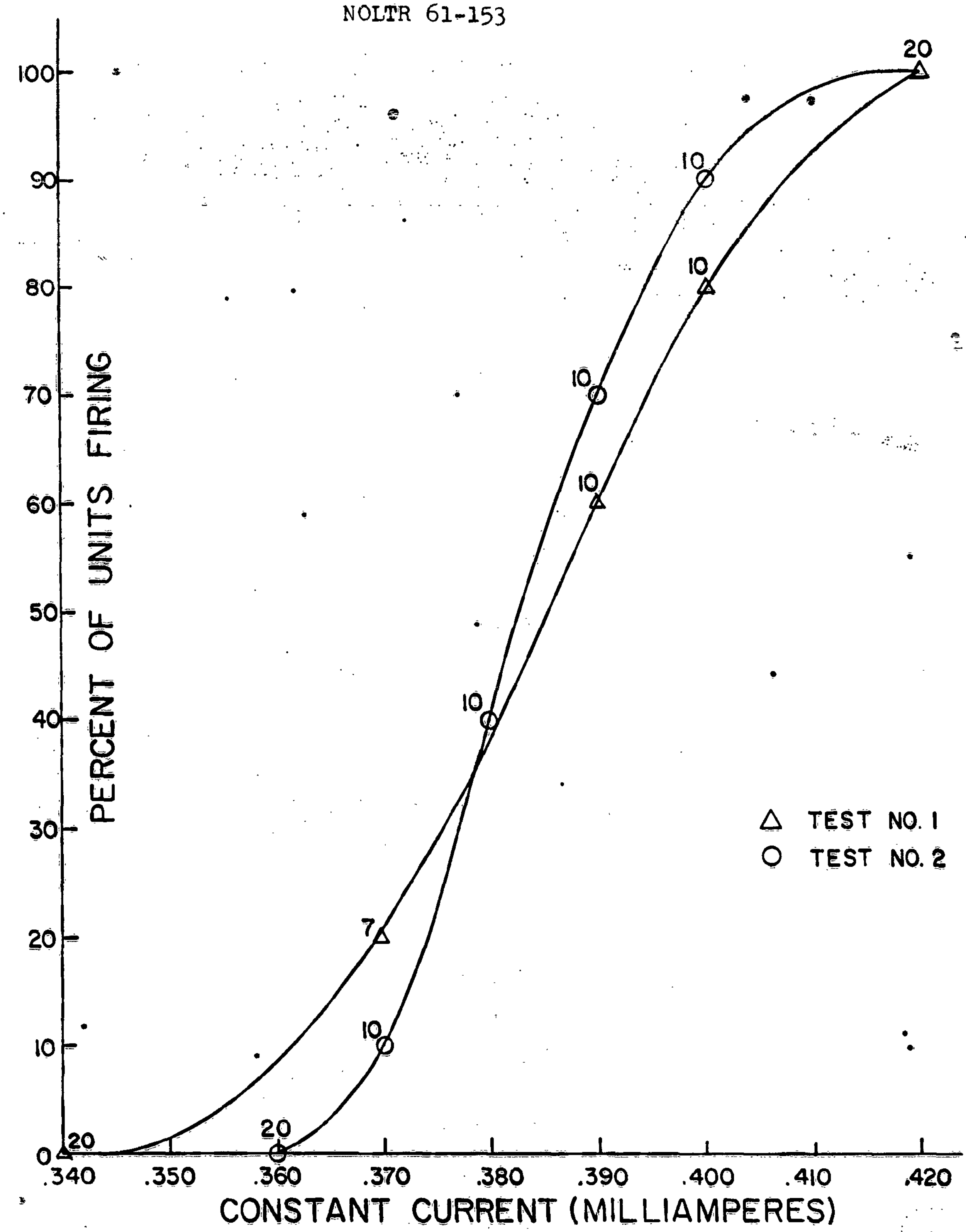

FIGURE 4. PERCENT FIRING VS CONSTANT CURRENT FOR Zr/PbO 50/50 IGNITER MIX.

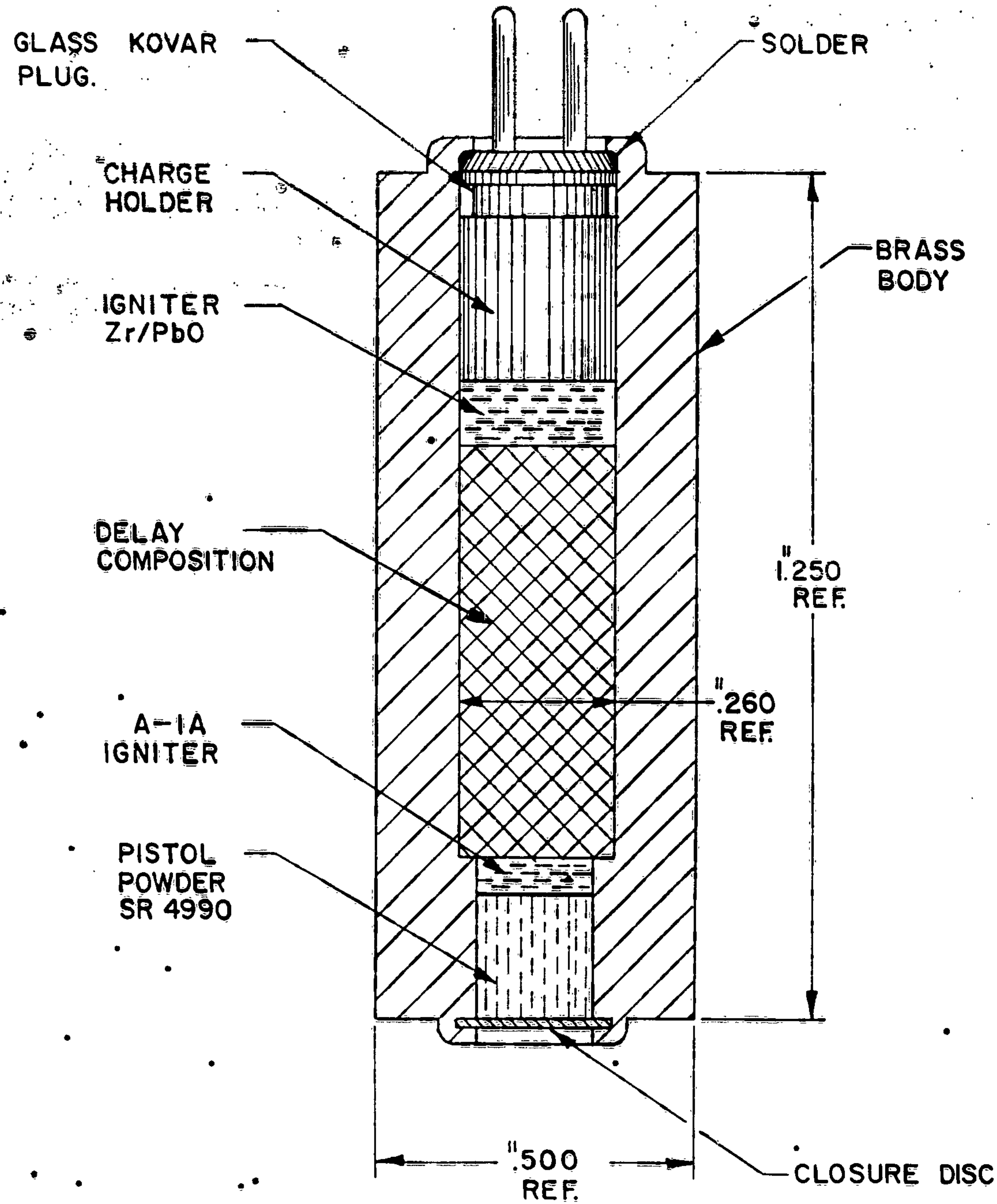

FIGURE 3. THE TEST VEHICLE USED FOR TESTING THE SLOW BURNING DELAY COMPOSITION.

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A LOW GASSING IGNITER MIXTURE FOR VARIOUS PYROTECHNIC DELAY COMPOSITIONS (U), by E. Eugene Kilmer. 1 Nov. 1961. 13p. charts, tables. Project RUME 3E000/212 1/F008 10 004, Problem 016. UNCLASSIFIED

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2. Igniters
3. Delay mixtures
4. Zirconium
5. Lead monoxide
6. Molydenum
7. Manganese
I. Title
II. Kilmer, E. Eugene
III. Project

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